APPLICATIONS OF X-RAY AND NEUTRON METHODS TO POROUS MANGANESE OXIDE SYSTEMS

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ABSTRACT

This presentation will focus on the use of X-ray and neutron methods for studying various microporous and mesoporous manganese oxide materials. The manganese oxide systems crystallize as either layered or tunnel structure systems. The initial stages of nucleation and structural phase changes that occur during aging and thermal treatment will be discussed. Both diffraction and scattering methods have been used in these systems. Complementary characterization methods include surface area, pore size distribution, scanning electron microscopy, and high resolution electron microscopy experiments.

INTRODUCTION

The synthesis of quantum size[1] porous semiconducting[2,3] manganese oxides has been accomplished by systematically varying the nature of organic cations which are used as structure directors.[4] One of the major precursors for preparation of manganese oxide materials is $KMnO_4$, which readily reacts with organic cations. This facile set of reactions has inhibited the synthesis of porous manganese oxides that contain organic moieties. We have focused on new synthetic routes to porous manganese oxides in the absence of inorganic cations. Stable colloids of layered manganese oxide materials can be prepared from reduction of tetraalkylammonium (tetramethylammonium, tetraethylammonium, tetrapropylammonium and tetrabutylammonium) permanganate salts. Such systems are interesting because particle size can be controlled, the colloids are extremely stable at room temperature, a variety of crystalline materials can result, and the initially formed phases can be interconverted into other phases. The particle sizes can be controlled from about 15 to 200 Å which allows systematic studies of nanocrystalline phase materials. Several aspects of these materials will be discussed including synthesis, characterization, and potential applications. Other related materials that have been prepared by using surfactants in order to generate mesoporous materials will also be described. The primary methods that have been used to understand these materials are X-ray powder diffraction and small angle neutron scattering methods.

EXPERIMENTAL

Samples were prepared by pipetting small amounts of the colloidal sol onto glass slides with concomitant evaporation of solvent prior to thin film formation, or by spreading thin layers of the sol onto glass slides. A Scintag XDS-2000 diffractometer with CuK_α radiation was used to obtain diffraction data. SANS data were collected on the time-of-flight small-angle diffractometer (SAD) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) methods were used to study the phases that formed during synthesis of the colloids and subsequent production of gels and heated gels. XRD patterns of various tetraalkylammonium cations reacted with permanganate led to production of well ordered systems after thermal treatment. The mesoporous materials typically produced broad diffraction data so that lattice parameters and structural models were developed with electron diffraction data from transmission electron microscopy methods.

The XRD data clearly show that expanded octahedral layer (OL) synthetic birnessite materials (OL-1) were produced in all cases. The originally formed colloids before heating were quite amorphous whereas thermal treatment even at mild temperatures (such as 70°C) led to production of well ordered phases.

Small angle neutron scattering (SANS) experiments clearly show that small nanoclusters of manganese oxide are formed at initial stages of reaction. We have used this information to stop the growth of such nanoclusters in order to use various size species to prepare other systems. By using SANS data for sols heated and aged to different extents it has been possible to prepare clusters of various sizes. Further support for the varying sizes of such clusters comes from UV-visible spectroscopy where growth of the clusters leads to a red shift in absorbance.

The interlayer structure of these materials shows that about 3 major types of structures can form. One structure involves intercalation of only the tetraalkylammonium cations in between the layers. Another structural type involves incorporation of the tetraalkylammonium cations as well as one layer of water molecules which increases the d-spacing between these layers. A further increase in d-spacing occurs when 2 different water layers are incorporated with the tetraalkylammonium cations in between the layers of OL-1.

The shapes of the colloids can be determined by modeling the SANS data. Several shapes were proposed and the best fit to the data analysis is a layered phase similar to OL-1. These layered disks are believed to be precursors for most of the octahedral molecular sieve (OMS) and octahedral layered materials of porous manganese oxides that have been prepared.[5] Several other factors are in line with this observation. First of all, the most common mineral of manganese oxide is the layered structure birnessite. Synthetic birnessite with small particle sizes is OL-1, which seems to always form in syntheses of OMS and OL materials. Secondly, calorimetric studies[6] also suggest that birnessite and OL materials have lower heats of formation than any other porous or nonporous manganese oxide mineral or synthetic material.

The mesoporous manganese oxide systems that have been prepared also seem to grow from this initial layered phase.[7,8] Certainly other factors are important in such syntheses such as the average oxidation state of manganese, the nature of the surfactant used in the synthesis, and the solvent.

The average manganese oxidation state in these systems is often around 3.6 or 3.7 as determined by titration and X-ray absorption studies. The reduction of Mn^{4+} to Mn^{3+} and Mn^{2+} leads to mixed valency, which in turn gives rise to enhanced conductivity of these materials. The semiconducting nature of these particulates allows experiments where charging problems can occur to be done more readily. Some examples include surface analyses by Auger electron spectroscopy, X-ray photoelectron spectroscopy and morphological studies by scanning and transmission electron microscopy. Such morphological studies have confirmed the generation of layered structures, although at times fibrous structures can be observed.[4-8]

CONCLUSIONS

XRD and SANS studies have provided a wealth of information about porous manganese oxide materials such as the nature of the size and shape of particulates, stability, thermal effects, and the mechanism of crystal growth. Such studies are in line with the generation of layered nanoclusters of manganese oxide similar to birnessite, which can grow and aggregate into other structures.

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